SUBSTITUTED 1,10-PHENANTHROLINES AS SPECIFIC REAGENTS IN ANALYTICAL CHEMISTRY

BY

WARREN WILLIAM BRANDT

B.S., Michigan State College, 1944

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1949

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PART I.

SUBSTITUTED 1,10-PHENANTHROLINES AS SPECIFIC REAGENTS IN ANALYTICAL CHEMISTRY

Introduction

The use of volumetric oxidation-reduction reactions in analytical chemistry is continually increasing. The developments in the field have been advanced over a period of several decades. A desirable step in the continued advancement of analytical chemistry would be the introduction of a series of oxidation-reduction indicators which would fill the gaps in the table of potentials available.

To accomplish such a purpose by any method but a completely random search would require some basic type of compound in which predictable variations of a desired character could be accomplished. Such a system has not been reported.

It is the purpose of the present investigation to develop, by systematic substitution of the parent compound, a series possessing these desirable properties. It is proposed to extend this series of compounds to other useful determinations in the field of analytical chemistry, and to suggest how further compounds may be synthesized to give predictable desired properties.

Experimental

A series consisting of the twenty-four methyl-substituted phenanthrolines listed in Table I was investigated with respect to their oxidation-reduction potentials, spectrophotometric constants, relative basicities, relative instabilities, and applicability as specific anion precipitants. The compounds studied were synthesized and furnished through the cooperation of Professor Francis H. Case of Temple University (1).

TABLE I

METHYL SUBSTITUTED 1,10-PHENANTHROLINES INVESTIGATED

Mono-	Di-			Tri-		Tetra-
3	3,4	4,5	5,6	3,4,6	3,5,8	3,4,6,7
4	3,5	4,6		3,4,7	3,6,7	3,4,6,8
5	3,6	4,7		3,4,8	4,5,7	3,4,7,8
	3,7			3,5,6		3,5,6,8
	3,8			3,5,7		

The oxidation-reduction potentials were determined by the titrimetric method. Reference points for the Fe(III) - Fe(II) and Ce(IV) - Ce(III) systems were obtained in order to substantiate the values obtained. The spectrophotometric examinations were made on a G. E. Recording Spectrophotometer. The wavelength of maximum absorption of the ferrous and ferric complexes was determined. The molecular extinction coefficients of the ferrous systems were calculated.

The apparent K_a of the protonated organic ions were determined by pH measurements. By comparison of the relative decomposition in high pH buffers, a scale of relative stability of the ferrous complexes was established.

Applications as specific anion precipitants were investigated by a semi-quantitative spot plate technique. The insolubilities of the precipitates of various anions were compared to similar compounds which might be possible interferences.

SUMMARY

A series of oxidation-reduction indicators covering the range 0.8-1.10 volts has been developed. The variations are the result of various substitutions of the 1,10-phenanthroline molecule. The effect of a substituent in a certain position can be accurately predetermined. This represents the first reported case in which an accurate prediction can be made concerning the effect of substitution of an organic molecule upon analytical properties.

This predictability is not limited to the oxidation-reduction potentials, but it is applicable to the spectrophotometric constants. It holds also in the consideration of the relative basicities of the organic molecules and the relative instabilities of the complexes.

The sensitivity of the ferroin reaction as a colorimetric method for the determination of iron has been increased. The wavelength of maximum absorption of the ferrous complexes has been varied from 496-520 millimicrons. The ferric complexes give values between 560 and 690 millimicrons. The substituted ferroins have been shown to be desirable reagents as anion precipitants. Their specificity as precipitation reagents for perchlorate, periodate, peroxydisulfate, thiocyanate, and fluotantalate has been demonstrated by a comparison of the insolubility of these anions with that of common interfering ions.

Correlations have been pointed out relating the oxidation-reduction potential, the relative basicity, and the relative instability to the changes in the electron density distribution around the nitrogen atoms in the molecule.

PART II.

SOME CHELATE COMPLEX SALTS OF RUTHENIUM

Introduction

Tris-dipyridyl ruthenium(II) chloride hexahydrate has been applied as an oxidation-reduction indicator to the titration of oxalate with perchloric acid solutions of cerium (IV) by Steigman (5). He reports the oxidation-reduction potential to be 1.33 volts in 1.0 N nitric acid. Dwyer (2) has investigated the related tris-1,10-phenanthroline ruthenium (II) complex and found its oxidation-reduction potential to be 1.29 volts in the same acidity.

This data is contrary to the expected by analogy to the

ferrous complexes. In order to explain this apparent increase in stability of the dipyridyl complex over that of the 1,10-phenanthroline, Dwyer postulated that actually no contradiction occurred. He based the apparent lower stability of the 1,10-phenanthroline complex upon the oxidation of the organic molecule by cerium (IV).

Experimental And Results

The oxidation-reduction potentials for the system studied by Steigman were determined by the titration method. Values were obtained in 0.1 F - 16.0 F hydrogen ion concentrations. The value in 1.0 N nitric acid was 1.25 volts. This value corrects the one presented by Steigman. The effect of the chloride present may have caused his reference point to be in error. Thus there is no anomaly concerning the relative stability of the dipyridyl and ortho-phenanthroline complexes of ruthenium (II).

A study of the mixtures of cerium (IV) and ortho-phenanthroline in nitric acid indicated that under certain conditions the oxidation of the ortho-phenanthroline does occur. The decomposition starts slowly and becomes more rapid toward the end. This explanation alone is insufficient to explain the observed instability of the ruthenium (III) complex of 1,10-phenanthroline.

PART III.

CRYSTALLOGRAPHIC INVESTIGATION OF COMPOUNDS $M_2Ce(NO_3)_6$

Introduction

An x-ray investigation of certain ceric nitrate salts was undertaken with the eventual purpose of deciding on their crystal structure. The problem is interesting since there has been some dispute as to the nature of these salts (4). There

are reasons to believe that in the crystalline state the hexanitrato-cerate radical can exist. It is difficult to account for a mixed salt, in the ordinary sense, when the single components can not be prepared. The preparation of ceric nitrate has not been reportel.

Two forms of the potassium hexanitrato-cerate and one form of the ammonium salt are reported in the literature (3). One reported form of the potassium salt is monoclinic and the other hexagonal.

Experimental And Results

Two forms of the potassium hexanitrato-cerate have been isolated. This represents the first occasion that both forms have been reported by one author. One form is found to be monoclinic and has no water of crystallization. The other form is hexagonal. This latter form is very difficult to obtain in a dry form, and is presumed to be the hexagonal form described in the literature containing 1½ molecules of water of crystallization.

Weissenberg and Buerger precession techniques were employed for the x-ray investigation of these salts. The monoclinic form was found to possess parameters a:b:c = 8.27: 6.64 : 12.66 A. and $\beta = 91°$. The density was found to be 2.66. This permits a calculation giving a value of two molecules per unit cell. The space group is $P2_1/n$. The hexagonal form has axial ratios a : c = 1 : 1.27.

The well known ammonium salt was found to be monoclinic as reported. The parameters are a : b : c = 8.14 : 6.75 : 13.05 and $\beta = 91°$. Using the known density, a value of two molecules per unit cell is calculated. The space group is $P2_1/n$.

A $P2_1/n$ space group with two moleculees in the unit cell requires that the molecule have a center of symmetry. It is difficult to conceive of an arrangement of a potassium nitrate-ceric nitrate double salt with a center of symmetry. This would indicate that the hexanitrato-cerate radical does exist in the

crystalline state. Considering the high density of the compounds, a very close packing must exist. An octahedral arrangement of the nitrate groups is highly probable.

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VITA

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The author is a member of the American Chemical Society, Sigma Xi, Phi Lambda Upsilon, and Phi Kappa Phi.